STRUCTURAL CHARACTERIZATION OF POLYMERS FOR ENERGY AND BIOMEDICAL APPLICATIONS (SANS)

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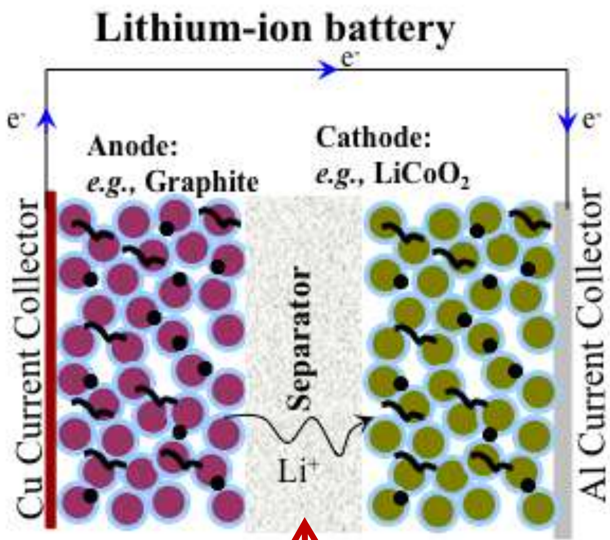
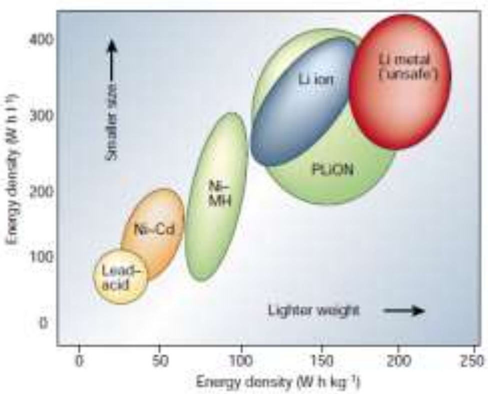
Li-ION BATTERIES: WORKHORSE IN MANY APPLICATIONS

Anode:
- Carbon-based
- Alloys and intermetallics
- Oxides



Cathode:
- Transition-metal oxides
- Spinel-based
- Olivine-based



Electrolyte:
- Liquid organic solvents
- Polymers
- Gels
- Ionic liquids

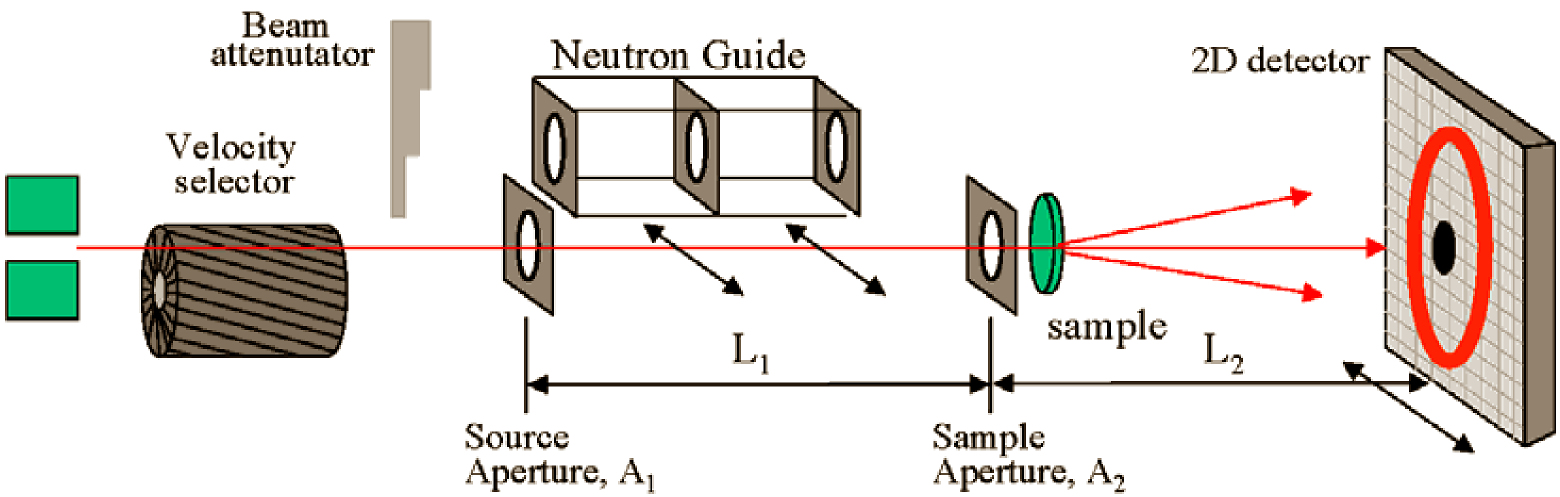
Solid polymer electrolytes

- **Safety (nonflammable, electrochemically stable)**
- **High energy density**
- **Improved lifetime**

- **Low ambient temperature conductivity**
- **Low Li transference**
- **High interfacial impedance**

Glassy polymers grafted with PEO are promising candidates as high-performance and safe electrolytes

Small Angle Neutron Scattering (SANS)



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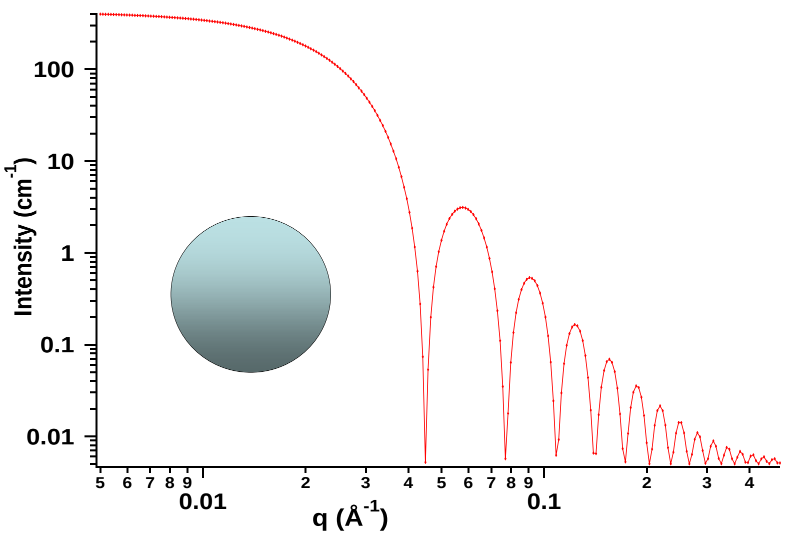


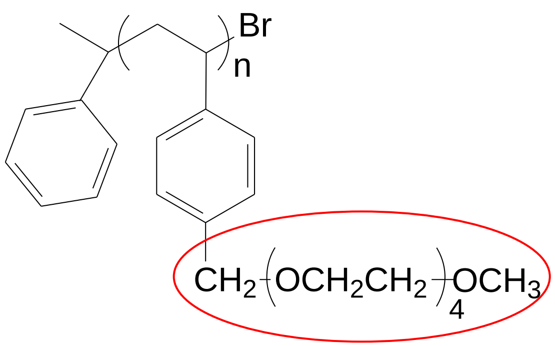
$$\frac{d\Sigma(q)}{d\Omega} = \Delta\rho^2 V_P{}^2 N_P P(q) S(q)$$

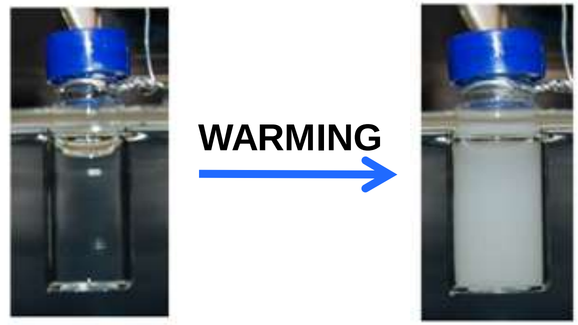
Where Δρ is the contrast factor; V_P is the particle volume; N_P is the number density of the particles

$$q = 4\pi \sin\theta / \lambda$$

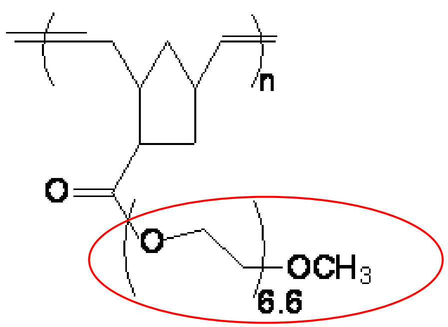
Length scale ~ 1/q : 10 to 1000Å

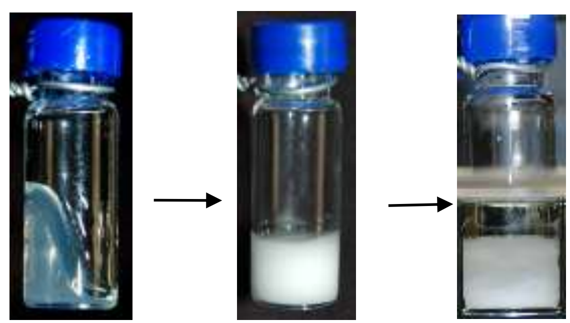
Newly synthesized OEG-Grafted polymers





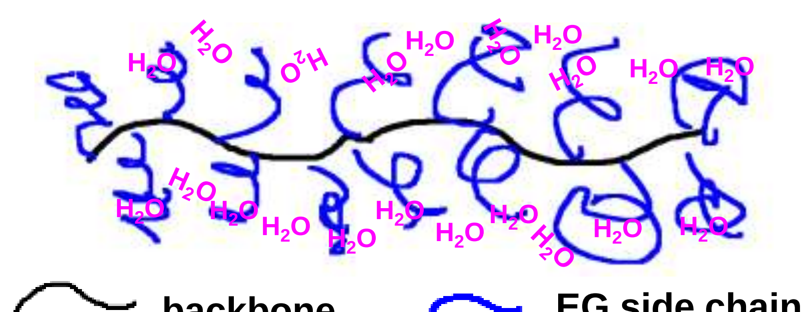
No EG GROUPS	Cloud point (T °C)
3	12
4	39
5	55
7	82





SOL GEL PRECIP

COMB-LIKE POLYMERS



1) Hydrophobic/hydrophilic
2) Phase separation upon heating in water
3) Gelation at high polymer concentration

Form Factors

1) The form factor of a rigid cylinder with a cross section radius R and length $2H$ is given as :

$$P(q) = \int_0^{\pi/2} [2 j_0(qH\cos\alpha)\frac{J_1(qR\sin\alpha)}{qR\sin\alpha}]^2 \sin\alpha d\alpha \qquad \text{(A1)}$$

Where $V_{cyl} = \pi R^2 L$ and $H = L/2$. $j_0(x) = \sin x / x$ and J_1 is the first order Bessel function.

2) The form factor of an ellipsoid with axes r_a, r_b and r_b is given as :

$$P(q) = \frac{\phi}{V_{ell}}(\rho_{ell} - \rho_{solv})^2 \int_0^1 F^2[qr_b(1 + x^2(v^2 - 1))^{1/2}]dx \qquad \text{(A2)}$$

Where $F(z) = 3V_{ell}\frac{\sin z - z\cos z}{z^3}$, $V_{ell} = \frac{4\pi}{3} r_a r_b^2$, $v = \frac{r_a}{r_b}$.

Guinier, A.; Fournet, G. In Small-Angle Scattering of X-Rays, John Wiley and Sons: New York, 1955.

Form Factors

3) The form factor of a semi flexible cylinder with the contour length $L \le 4b$, where b is the Kuhn length, and a cross section radius R is given as follows:

$$P(q,L,b) = P_{chain}(q,L,b)[2J_1(qR)/(qR)]^2 \qquad \text{(A3)}$$

For $qb \le q_0(L,b)$, where $q_0 = \max\{1.9/<R_g{}^2>^{1/2}, 3\}$

$$P_{chain}(q,L,b) = 2[\exp(-u)+u-1]/u^2 \qquad \text{(A4)}$$

Where $u = R_g{}^2 q^2$, $R_g = <R_g{}^2>^{1/2}$, $<R_g{}^2> = \alpha(L/b)^2 <R_g{}^2>_0$,

$\alpha(x)^2 = [1+(x/3.12)^2 + (x/8.67)^3]^{0.170/3}$,

$$<R_g{}^2>_0 = \frac{Lb}{6}[1 - \frac{3}{2n_b} + \frac{3}{2n_b{}^2} - \frac{3}{4n_b{}^3}[1-\exp(-2n_b)]],\ n_b = L/b$$

For $qb > q_0(L,b)$,

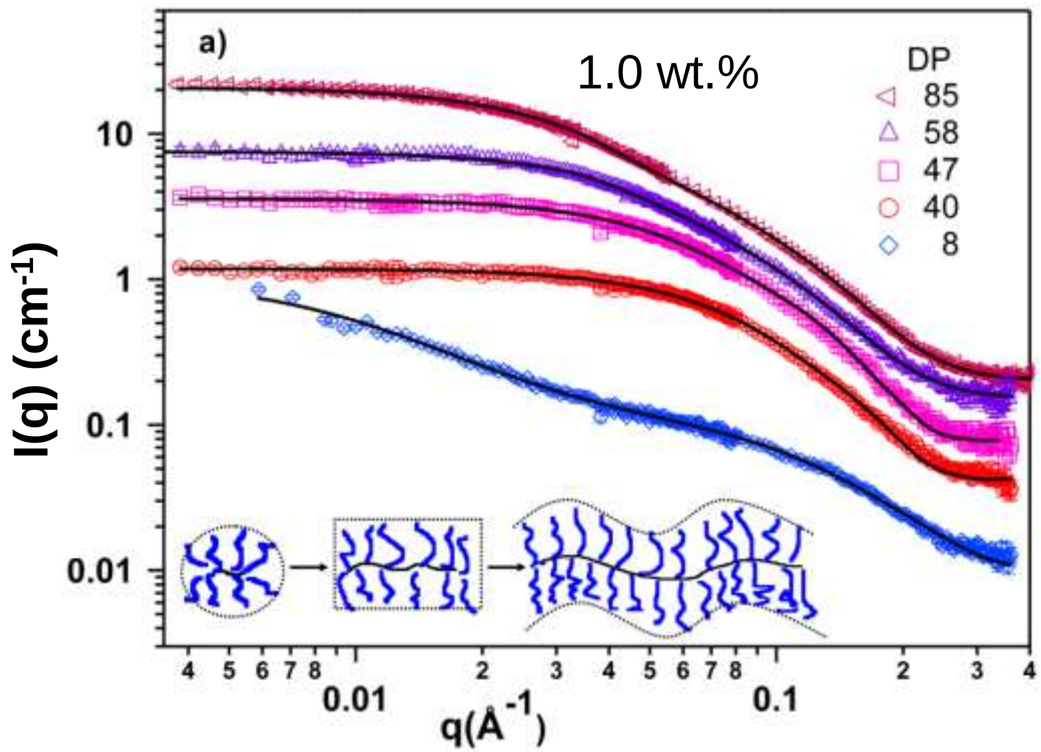
$$P_{chain}(q,L,b) = \frac{a_1}{(qb)^{p_1}} + \frac{a_2}{(qb)^{p_2}} + \frac{\pi}{qL} \qquad \text{(A5)}$$

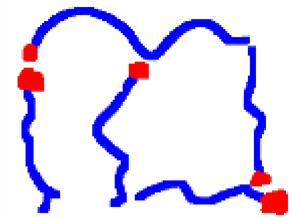
Where p_1 and p_2 are empirical constants and $p_1 = 5.36$, $p_2 = 5.62$.

1. Pedersen, J. S.; Schurtenberger, P. Macromolecules 1996, 29, 7602.

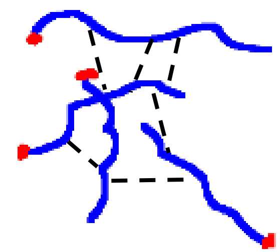
2. Chen, W.-R.; Butler, P. D.; Magid, L. J. Langmuir 2006, 22, 6539.

POLYMER CONFORMATION IN D-TOLUENE AS A FUNCTION OF THE BACKBONE LENGTH





End group interactions



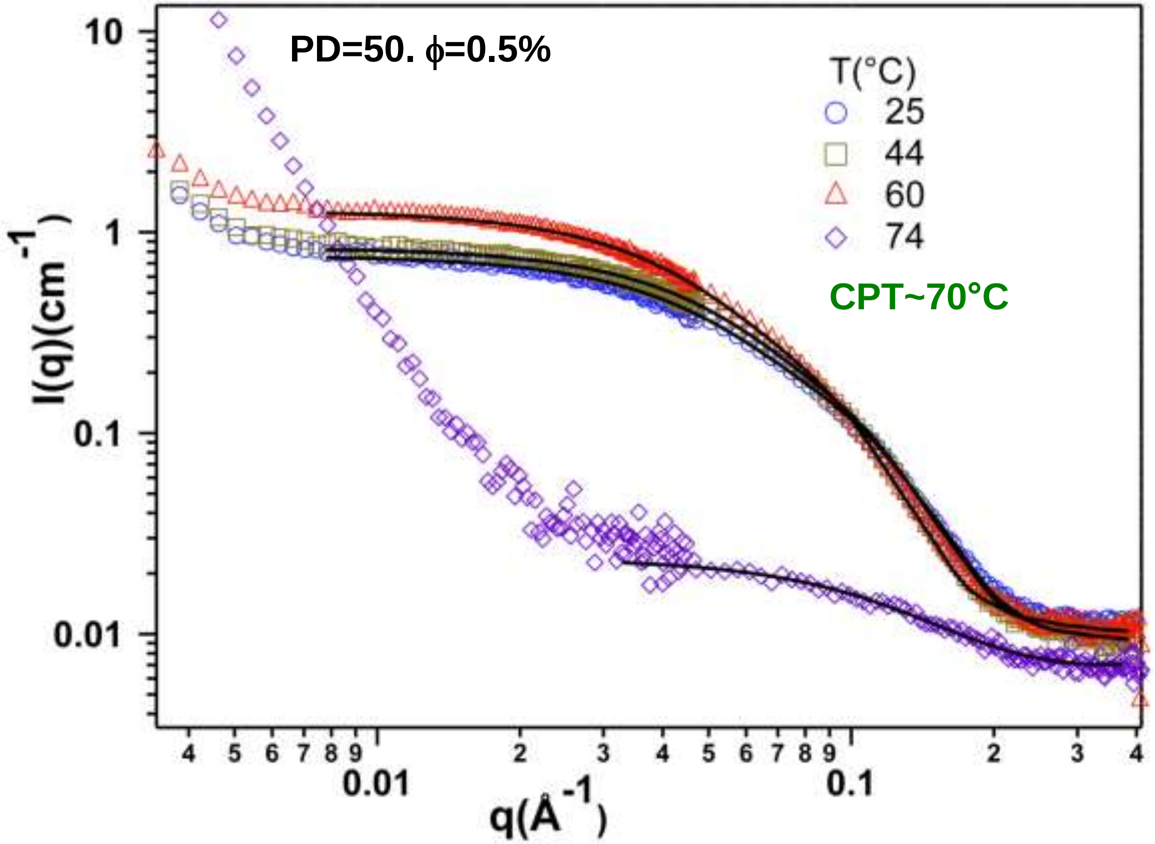
Hydrogen bonding ?

- Shape transition with DP
- Clusters in solutions of polymers with a DP=8
- Solid lines are fits to form factors of an ellipsoid, rigid cylinder or a semi-flexible cylinder

VARIATION OF THE CONFORMATION WITH TEMPERATURE (SOLUTIONS IN D_2O)

Zimm equation

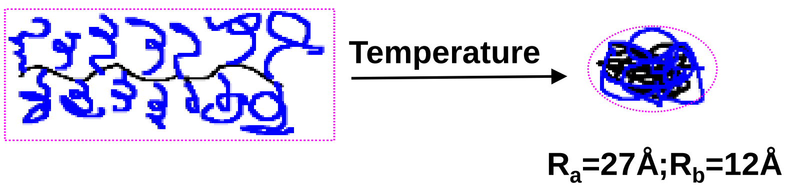
$$I(q) = \frac{c}{K} \frac{\overline{P(q)}}{1 + 2cA_2 M_w \overline{P(q)}} + bkg$$



- A rigid cylinder form factor was able to fit the data at 25, 44 and 60° C
- An ellipsoid form factor was able to fit the high q portion of the data at 74° C

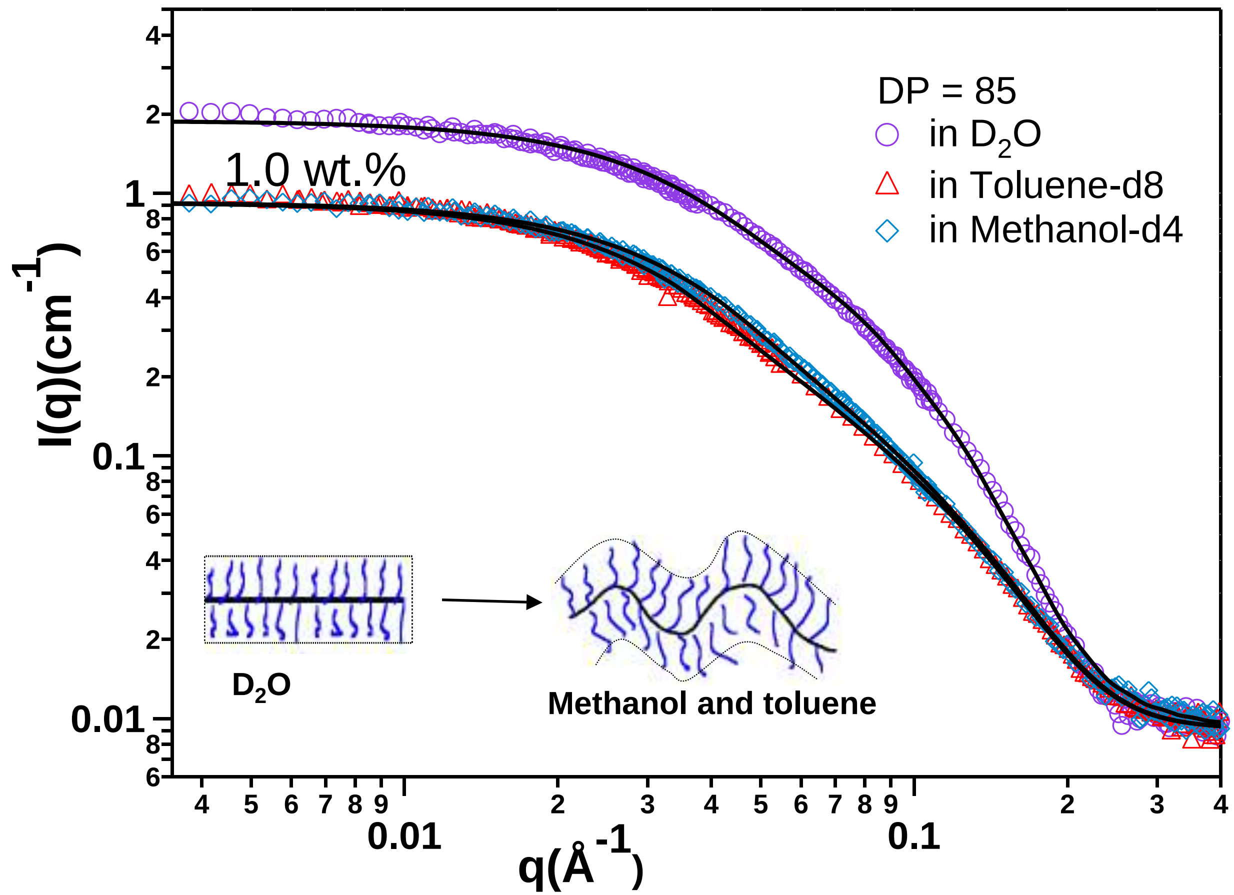
Fitting results

25°C			44°C			60°C		
C(wt.%)	*R*(Å)	*L*(Å)	*C*(wt.%)	*R*(Å)	*L*(Å)	*C*(wt.%)	*R*(Å)	*L*(Å)
0.1	15	113±1	0.1	16	102±1	0.1	16	98±1
0.5	15	113±3	0.5	17	97±3	0.5	17	104±3
1.0	15	116±4	1.0	16	106±3	1.0	16	113±6
2.0	16	118±6	2.0	16	119±6	2.0	16	92±17



Polymers contracts slightly near the cloud point temperature and collapse to ellipsoids at 74° C

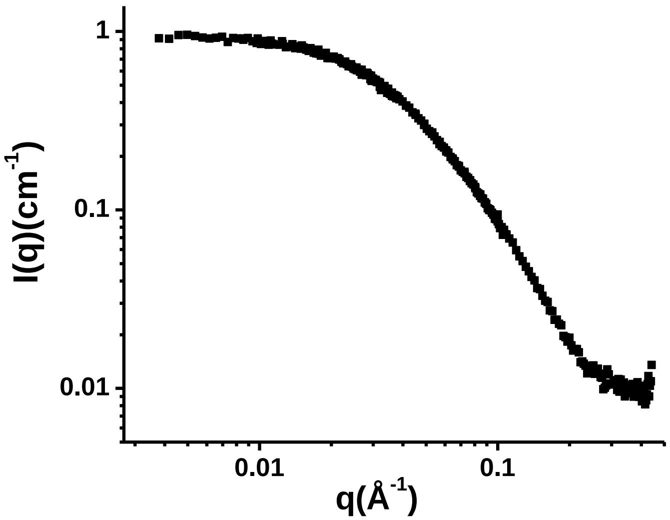
Polymer conformation in different solvents

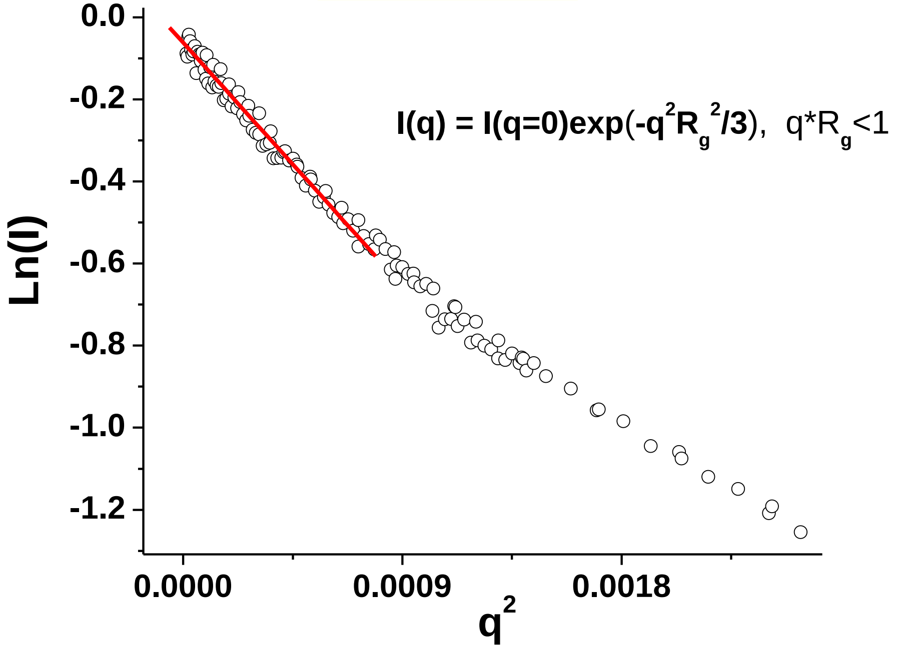


• Polymers assume rigid cylinders in D_2O while they take semi-flexible cylinders in methanol and toluene

In D_2O: R=13Å, L=135Å;
In toluene: R=10Å, L=230Å, Kuhn length=90Å;
In methanol: R=10Å, L=216Å, Kuhn length=73Å

Guinier Plot: Ln(I(q)) vs q^2





- Guinier plot, Ln(I) vs q^2 , is independent of the shape of the particles
- I(q=0) and Rg can be obtained from the Guinier Plot

Second viral coefficient A_2 IN D_2O

$$A_2 = -\frac{2\pi N_A}{{M_w}^2}\int_0^\infty (\exp(-W(r)/kT) - 1) r^2 dr$$

W(r): average interactions between two particles at infinite dilution

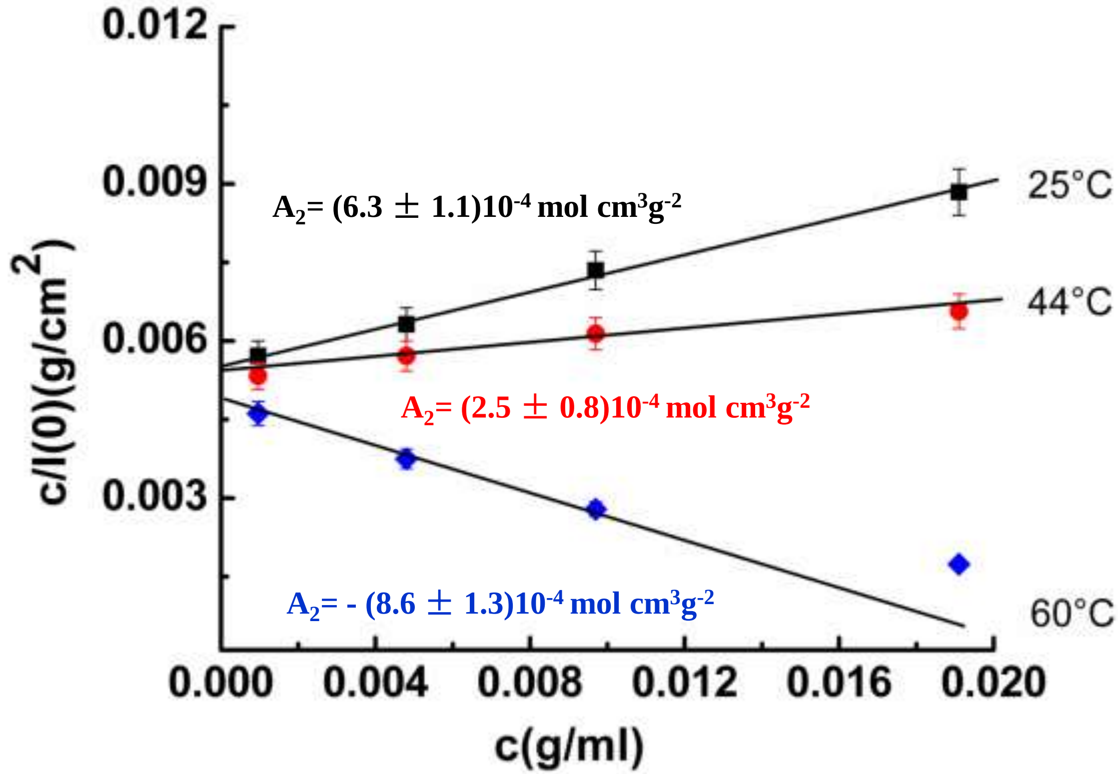
$A_2 > 0$, repulsive interactions

$A_2 < 0$, attractive interactions

Zimm plot

$$\frac{c}{I(0)} = K(1 + 2A_2 c M_w)$$

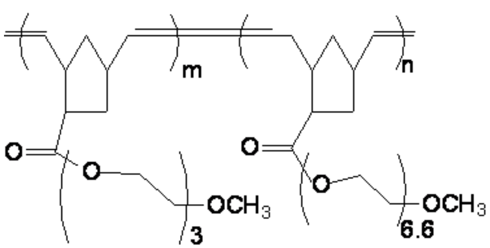
I(0) is obtained via Guinier Plot

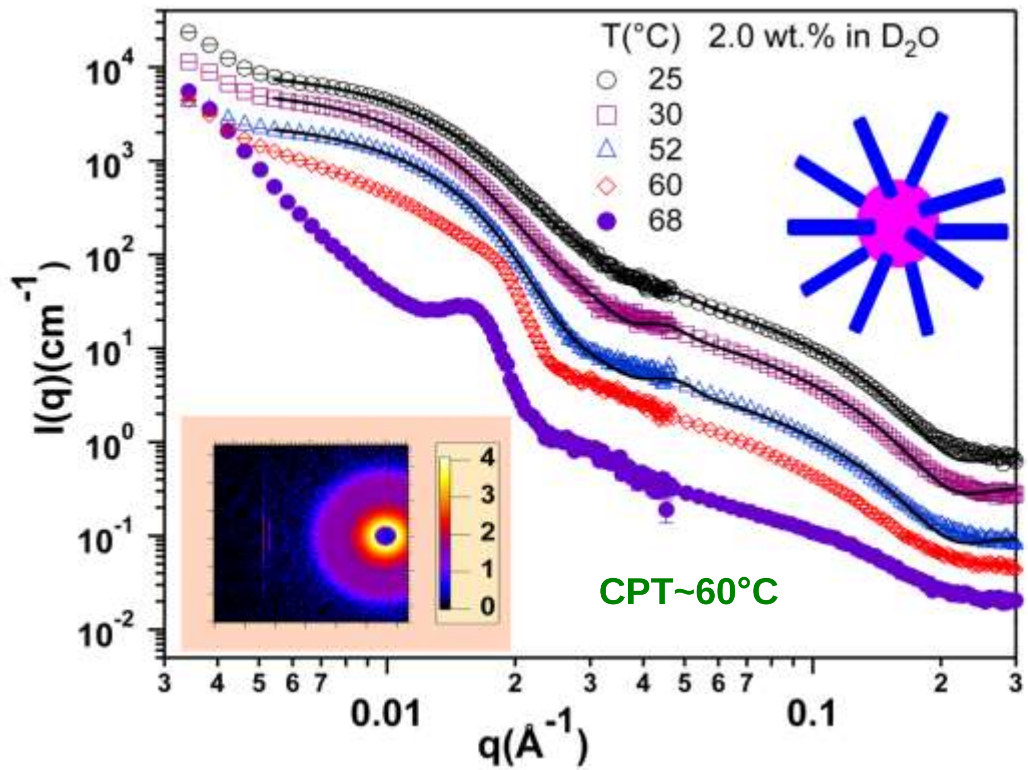


Block copolymers in D_2O

MULTIPHASE MATERIALS TO DECOUPLE STRUCTURAL ELEMENTS RESPONSIBLE FOR HIGH CONDUCTIVITY AND MECHANICAL PROPERTIES

$(EG_{3.0}NB)$ -b-$(EG_{6.6}NB)$





$$F_{Micelle}(q) = N_{agg}^2 \beta_{core}^2 \Phi(q)^2 + N_{agg} \beta_{chain}^2 Fcyl(q) + N_{agg}(N_{agg} - 1)\beta_{chain}^2 A_{chain}^2$$

$$+ 2N_{agg}^2 \beta_{core} \beta_{chain} A_{chain}(q)\Phi(q)\Phi$$

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